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Structural studies on trifluoromethyl substituted 2,5-diphenyl-1,3,4-oxadiazoles

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Abstract

Three new compounds have been synthesized based on the molecular motif 2-[2,6-bis(trifluoromethyl)phenyl]-5-phenyl-1,3,4-oxadiazole, with subsequent CF_3-substitution in the *ortho*-positions of the phenylene ring. The crystal structures of the compounds have been determined by single crystal X-ray diffraction. All compounds have a monoclinic structure. The solid state structure of the compounds is influenced by the electronic properties of the fluorine atoms, leading to the occurrence of C–H···F, and C–F···π interactions, partly replacing π–π interactions usually observed in the crystal structures of 2,5-diphenyl-1,3,4-oxadiazole derivatives. Other significant interactions than those involving fluorine appear only in rare cases. The strong impact of the fluorine atoms on the intra- and intermolecular interactions, and the molecular conformation lead to novel inputs for the understanding of molecular recognition, supramolecular assembly, and crystal packing of fluorine containing compounds.

Keywords: Crystal structure; 1,3,4-oxadiazole; Molecular conformation; Weak interactions

1. Introduction

Due to their structural variability organic materials offer many possibilities to tune their properties to actual needs and to become versatile high tech materials with a broad application spectrum. Aromatically substituted 1,3,4-oxadiazoles are widely used as scintillators, fluorescence and photographic materials [1,2] or for non-linear optical applications, but they are also known as biologically active agents [3]. With the development of organic light emitting diodes these materials obtained a specific interest as electron transport and injection or, more important, as hole blocking layers [4–7] as well as emitting layers [8]. Oxadiazole containing materials are also interesting candidates for the use in thin-film-transistors.

The design of compounds with novel and improved chemical and physical properties as advanced functional materials with a specific application spectrum requires the knowledge about possible supramolecular packing motifs and their experimental control. This is one of the main topics of crystal engineering. Besides the structure of the individual molecule also non-covalent interactions play a significant role for the molecular conformation, the formation of a certain three-dimensional supramolecular architecture of a crystal as well as for molecular recognition processes, bioactivity etc. Functional groups may contribute to the formation of a specific packing motif due to their definite interactions. In their entirety the strength and directionality of these interactions create the characteristic supramolecular synthons which can be used for the design of supramolecular arrangements by the development of

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appropriate strategies for the precise control of the topology. Such non-covalent interactions are the characteristic π-stacking or hydrogen bonds that both have been extensively studied. If the molecules contain halogen atoms also halogen···halogen, C–H···halogen, or halogen···π interactions contribute to the formation of specific motifs. Such interactions have been studied recently for a variety of model compounds experimentally as well as by theoretical considerations (see for instance [9–15]). But they are still a matter of interest and discussion since halogen···π interactions are not commonly observed and their role in molecular recognition is not understood in detail yet [9]. A specific problem seems to be the presence of organic fluorine, whose behavior is different from that of the other halogen atoms [16,17]. The introduction of a fluorine atom leads to a modification of the packing motif compared to that of the non-fluorinated counterpart [12]. Nevertheless, although the interactions between fluorine atoms and C–H groups or π systems are weak they also contribute to the stability of the crystal structure, especially in the absence of other, strong interactions like hydrogen bonding, π–π or C–H···π interactions [12]. However, the use of such synthons to predict possible supramolecular arrangements is less developed.

In the following solid state structures of some newly synthesized heteroaromatic compounds containing the trifluoromethyl group will be presented as a contribution to broaden the knowledge about the fluorine···π interactions, the associated synthons and resulting characteristic packing motifs. The basic molecular structure is the 2,5-diphenyl-1,3,4-oxadiazole core. This study continues a series of previous investigations [18–21] where crystal structures for several differently substituted diphenyl-1,3,4-oxadiazole compounds have been investigated to derive common motifs and characteristic differences of the crystal packing with varying molecular structure. Familiar structural features for compounds with substitution in *para* position are planar or nearly planar molecules. This picture changes if the substituent is located in *ortho* position as could be shown in [20] for fluorine substitution. Here, the torsion angle between the central oxadiazole ring and both phenylene rings increases remarkably. The most obvious common packing motif is the occurrence of molecular stacks in most of the analyzed crystal structures. Within these stacks intense π–π interactions dominate between adjacent molecules between oxadiazole ring (acceptor) and phenylene rings (donor) although also deviations from this basic scheme may be found. The intermolecular interactions between the stacks are preferentially van der Waals forces or dipole–dipole interactions.

A series of fluorine containing, symmetrically substituted diphenyl-1,3,4-oxadiazoles has been studied recently [20]. Both phenyl rings were substituted by one fluorine atom in *ortho*, *meta*, and *para* positions, respectively. The resulting crystal structures were compared to that of the completely fluorinated compound. All structures differ in relation to the unsubstituted diphenyl-1,3,4-oxadiazole [19], although also some common motifs may be found. In the bis(monofluorophenyl) compounds mainly intermolecular π–π interactions determine the packing motifs accompanied by C–H···F interactions. While both, *para* and *meta* compounds, show π–π interactions between phenylene and oxadiazole rings of adjacent molecules, stacking interactions are restricted to the oxadiazole rings in the *ortho* compound. Molecular stacks are found for *meta* and *ortho* substitution, the *para* substitution is characterized by the occurrence of molecular layers with chains of molecules connected by C–H···F contacts. Interestingly, no π interactions are observed for the completely fluorinated compound. Here, the crystal structure is stabilized by close fluorine–fluorine contacts. Additionally, also fluorine···π interactions occur between fluorine atoms and the central oxadiazole ring.

This substitution also influences the planarity of the molecule. The *meta* compound is considerably flat with dihedral angles of approximately 6° and 4° between both phenylene rings and the oxadiazole ring. The *para* and the *per*fluorinated compounds show increased values with 13°/16° and 14°/14°, respectively, while the *ortho* substitution leads to the largest deviation from planarity (29°/29°).

All of these compounds only contain fluorine atoms as substitutents. In the following, a more bulky group, the trifluoromethyl group, is introduced into the basic diphenyl-1,3,4-oxadiazole molecule as substituent. All three subsequently investigated derivatives contain the trifluoromethyl groups in the *ortho* positions of the phenylene rings. Compound OXA1 (2-[2,6-bis(trifluoromethyl)phenyl]-5-phenyl-1,3,4-oxadiazole) contains two CF_3-substituents only on one phenylene ring, while compound OXA2 (2-[2,6-bis(trifluoromethyl)phenyl]-5-[2-(trifluoromethyl)phenyl]-1,3,4-oxadiazole) and compound OXA3 (2,5-bis[2,6-bis(trifluoromethyl)phenyl]-1,3,4-oxadiazole) contain CF_3 groups on both rings, the latter in all four possible *ortho* positions. The aim is to give some new contributions for studies of the relations between molecular structure and crystalline packing motif. Molecular interactions between an aromatic π-electron system and fluorine atoms are an important topic in supramolecular chemistry. Therefore, the variations of the molecular conformation with the substitution scheme and the implications for the solid state structure will be investigated.

2. Experimental setup

2.1. Synthesis

The investigated trifluoromethyl group containing 2,5-di(phenyl)-1,3,4-oxadiazole compounds OXA1–OXA3 were synthesized using the classical procedure from tetrazole and the corresponding acid chlorides [22,23]. The products were dried in vacuum and repeatedly recrystallized from petrolether.

This synthesis procedure is outlined in more detail for OXA3, as prepared here for the first time. To obtain the tetrazole a mixture of 1 g (4.2 mmol) 2,6-bis(trifluoromethyl)phenylnitrile, 0.98 g (15 mmol) sodiumazide, and 2.05 g (15 mmol) triethylamine hydrochloride in 50 ml toluene is kept at 100 °C under stirring for 10 h. After cooling, the product is extracted

with water (4×50 ml). Concentrated hydrochloric acid is dropwise added to the aqueous phase and the resulting 5-[2,6-bis(trifluoromethyl)phenyl]tetrazole is salted out. After filtration, the white solid is washed with water and dried under vacuum (yield: 90%; Fp: 210 °C).

The corresponding oxadiazole compound OXA3 is synthesized by solving 1.04 g (37 mmol) of the tetrazole and 1 g (36 mmol) 2,6-bis(trifluoromethyl)benzoyl chloride in 15 ml dry pyridine. This solution is heated under reflux for 4 h, cooled and transferred into water. The precipitate is filtrated, dried and recrystallized from petrolether (yield: 90%; 99% purity by HPLC.)

2-[2,6-bis(trifluoromethylphenyl)]-5-phenyl-1,3,4-oxadiazole (OXA1): Fp: 102 °C, IR (ATR, cm^{-1}): 3087, 3069, 3038, 1607, 1590, 1575, 1551, 1483, 1462, 1451, 1343, 1298, 1261, 1217, 1180, 1138, 1124, 1070, 1048, 1023, 1005, 961, 923, 839, 823, 781, 764, 745, 705, 687, 676. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.08 (d, 2H, C7, C11), 8.06 (d, 2H, C14, C16), 7.88 (dd, 1H, C15), 7.48–7.58 (m, 3H, C8, C9, C10).

2-[2,6-bis(trifluoromethylphenyl)]-5-(2-trifluoromethylphenyl)-1,3,4-oxadiazole (OXA2): Fp: 96 °C, IR (ATR, cm^{-1}): 1593, 1570, 1539, 1468, 1460, 1452, 1343, 1316, 1294, 1273, 1255, 1210, 1186, 1176, 1145, 1133, 1116, 1069, 1037, 969, 961, 881, 838, 826, 773, 767, 759, 737, 711, 691, 677, 646. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.06 (d, 3H, C14, C16, C10), 7.89 (t, 2H, C15, C7), 7.85 (d, 1H, C10), 7.71 (t, 2H, C8, C9).

2,5-bis[2,6-bis(trifluoromethylphenyl)]-1,3,4-oxadiazole (OXA3): Fp: 177 °C, IR (ATR, cm^{-1}): 3104, 3071, 3037, 1593, 1578, 1567, 1456, 1345, 1294, 1251, 1214, 1187, 1151, 1131, 1068, 1035, 1007, 987, 842, 827, 759, 732, 710, 696, 677. ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] 8.06 (d, 2H, C14, C16), 8.06 (d, 1H, C10), 8.06 (d, 1H, C8), 7.89 (t, 1H, C15), 7.89 (t, 1H, C9).

2.2. X-ray structure determination

The crystal structures of OXA1–OXA3 have been determined by single crystal X-ray structure analysis. X-ray measurements of crystals of compound OXA1 and OXA2 were performed at 293(2) K on a Bruker AXS SMART/CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The reflection intensities of compound OXA3 were recorded at 293(2) K on an Enraf Nonius CAD4, using Mo-radiation. The structures were solved by direct methods using SHELXS-97 [24] and refined by full matrix least squares method using SHELXL-97 [25]. An empirical absorption correction (Ψ-scan) was applied. All non-hydrogen atoms were refined anisotropically. In case of compound OXA3 the positions of carbon-bound hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model. Isotropic displacement parameters of hydrogen atoms were derived from the parent atoms. Further experimental details are given in Table 1.

Crystallographic details on the structure analyses of the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC 609038–609040.

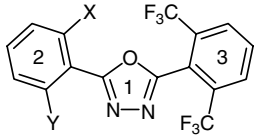

Fig. 1. Schematic representation of the substitution pattern in the investigated compounds. X,Y = H for compound OXA1; X = CF_3, Y = H for compound OXA2; X,Y = CF_3 for compound OXA3.

Table 1
Crystal data and structure refinements for the investigated compounds

	OXA1	OXA2	OXA3
Empirical formula	$C_{16}H_8F_6N_2O$	$C_{17}H_7F_9N_2O$	$C_{18}H_6F_{12}N_2O$
Formula weight	358.24	426.25	494.25
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, C2/*c* (No. 15)	Monoclinic, $P2_1/c$ (No. 14)	Monoclinic, $P2_1/c$ (No. 14)
Unit cell dimensions [Å, °]	$a = 26.828(4)$	$a = 12.084(2)$	$a = 9.313(2)$
	$b = 10.713(2)$	$b = 16.732(2)$	$b = 15.7248(14)$
	$c = 11.755(2)$	$c = 8.320(1)$	$c = 14.778(4)$
	$\beta = 115.834(3)$	$\beta = 103.447(7)$	$\beta = 122.606(8)$
Volume (Å^3)	3040.9(8)	1636.2(4)	1823.1(6)
Z, Calculated density (Mg/m^3)	8, 1.565	4, 1.730	4, 1.801
Absorption coefficient (mm^{-1})	0.150	0.180	0.198
F(0 0 0)	1440	848	976
Theta range for data collection (°)	2.08–25.00	2.12–25.00	2.09–28.37
Limiting indices	$-31 \leqslant h \leqslant 31$, $-12 \leqslant k \leqslant 11$, $-13 \leqslant l \leqslant 12$	$-12 \leqslant h \leqslant 14$, $-19 \leqslant k \leqslant 19$, $-9 \leqslant l \leqslant 9$	$0 \leqslant h \leqslant 12$, $-20 \leqslant k \leqslant 20$, $-19 \leqslant l \leqslant 16$
Reflections collected/unique	7312/2671 [$R_{(int)} = 0.0350$]	7888/2877 [$R_{(int)} = 0.0518$]	9725/4502 [$R_{(int)} = 0.1107$]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2671/0/259	2877/0/291	4502/0/299
Goodness-of-fit on F^2	0.969	0.967	1.144
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0446$, w$R_2 = 0.1376$	$R_1 = 0.0444$, w$R_2 = 0.1343$	$R_1 = 0.0677$, w$R_2 = 0.2174$
R indices (all data)	$R_1 = 0.0655$, w$R_2 = 0.1480$	$R_1 = 0.0444$, w$R_2 = 0.1343$	$R_1 = 0.1228$, w$R_2 = 0.2571$
Largest diff. peak and hole (e.Å^{-3})	0.290 and −0.299	0.234 and −0.230	0.469 and −0.411

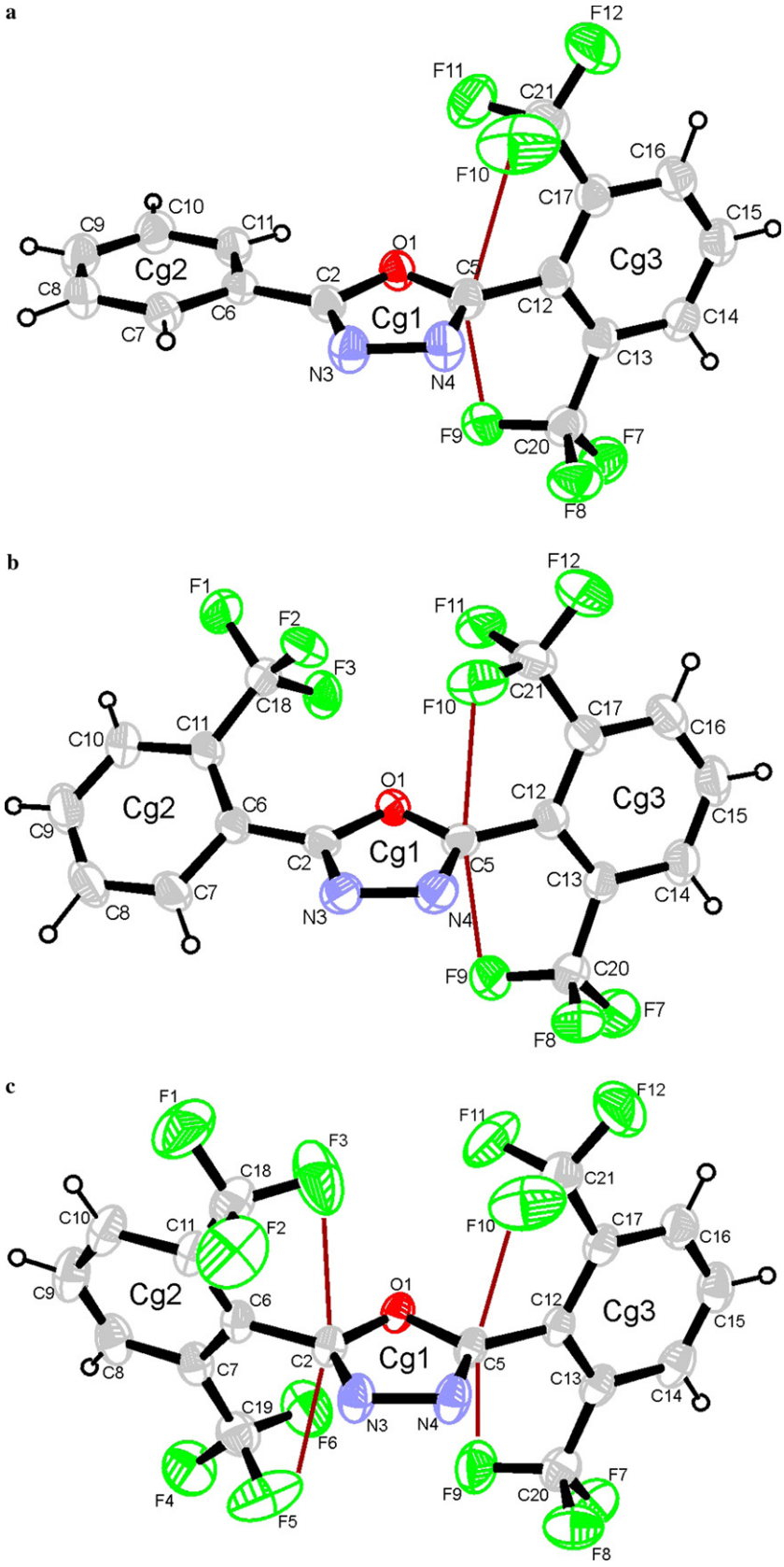

Fig. 2. The molecular structures of the investigated compounds OXA1 (a), OXA2 (b), and OXA3 (c) showing 30% probability displacement ellipsoids.

3. Results and discussion

3.1. Molecular conformation

Fig. 1 provides the schematic diagrams of the molecules referred to in the discussion, whereas Fig. 2 shows the ORTEP [26] plots of the molecules OXA1–OXA3. According to the X-ray diffraction data, each oxadiazole and phenylene ring in these molecules is perfectly planar in the crystalline state. The rms deviations from the mean planes are 0.0012 Å (ring 1), 0.0024 Å (ring 2), and 0.0057 Å (ring 3) for molecule OXA1, 0.0033 Å (ring 1), 0.0022 Å (ring 2), and 0.0112 Å (ring 3) for molecule OXA2, and 0.0025 (ring 1), 0.0082 Å (ring 2), and 0.0036 Å (ring 3) for molecule OXA3, respectively.

The conformation of the molecules can be described by the dihedral angles between the central oxadiazole and the adjacent phenylene rings. The angles between the planes as depicted in Fig. 1 are given in Table 2. Interestingly, the dihedral angle between the oxadiazole and phenylene ring 2 increases with the introduction of trifluoromethyl groups from nearly planar 6.7(1)° observed for OXA1 to an almost perpendicular orientation 81.8(2)° in OXA3. In all compounds studied the dihedral angles between the ring planes 1 and 3 remain nearly unaffected by the *ortho* substitutions in ring 2. The angle between the planes of the two phenylene moieties changes from nearly perpendicular 84.7(1)° in compound OXA1 to 50.8(1)° in OXA2 and 50.0(2) in OXA3.

The mean N–C distances of 1.271(3) Å of the discussed compounds confirm the double bond character between these atoms in the oxadiazole ring. The C–C distances for the bond between the oxadiazole and the phenylene rings range from 1.461(3) to 1.487(3) Å in good agreement with sp^2–sp^2 σ-bonds, indicating at least a very weak conjugation of the whole molecule. The mean C–F bonds in all compounds amount to 1.320(5) Å (OXA1), 1.332(7) Å (OXA2), and 1.327(8) Å (OXA3).

Intramolecular C–H···F interactions between the trifluoromethyl group and neighboring CH groups in the phenylene ring are observed for all three compounds. In case of compound OXA1 and OXA2 additional intermolecular hydrogen bonds including the oxadiazole oxygen (C11–H11···O1 with d(D···A) = 2.823(3) Å, d(H···A) = 2.50(2) Å, and ∠(D–H···A) = 100.3(18)°) and nitrogen (C7–H7···N3 O1 with d(D···A) = 2.877(3) Å, d(H···A) = 2.53(3) Å, and ∠(D–H···A) = 100.8(16)°), respectively, are formed.

The rotation of the CF_3 substituted phenylene rings with respect to the central oxadiazole ring gives rise to intramolecular C–F···π interactions listed in Table 4. As a measure of C–F···π interaction the distances between the fluorine atoms and the C atoms of the oxadiazole ring are considered. The shift values given in Table 3 indicate the deviation from a perpendicular arrangement of both atoms. As may be seen for the example of OXA2 and depicted in Fig. 2 the

Table 4
Intramolecular C–F···π electron interactions

Compound	F···C	D(F–C) (Å)	DP (Å)	Shift (Å)
OXA1	F9···C5	2.687(2)	2.652	0.432
	F10···C5	2.882(2)	2.760	0.830
OXA2	F9···C5	2.733(3)	2.704	0.396
	F10···C5	2.670(2)	2.617	0.530
OXA3	F3···C2	2.741(2)	2.680	0.575
	F5···C2	2.861(2)	2.691	0.972
	F9···C5	2.703(2)	2.666	0.446
	F10···C5	2.763(2)	2.687	0.644

Table 2
Conformation and intermolecular interactions in the crystal structures of OXA1–OXA3

Compound	Dihedral angles (°)	Dihedral angles (°)	Interring contact (Å)	Intramolecular interactions		Intermolecular interactions		
	Phenyl(2)-oxadiazole(1)/phenyl(3)-oxadiazole(1)	Phenyl(2)–phenyl(3)	phenyl(2)-oxadiazole(1)/phenyl(3)-oxadiazole(1)	C–H···F	C–F···π	π···π	C–F···π	F–F
OXA1	6.7(1)/79.7(1)	84.7(1)	1.461(3)/1.479(3)	+	+	+	+	–
OXA2	29.1(1)/69.8(1)	50.8(1)	1.471(3)/1.487(3)	+	+	+	+	+
OXA3	81.8(2)/78.0(2)	50.0(2)	1.486(2)/1.473(6)	+	+	–	+	+

Table 3
Intermolecular C–F···Cg interactions in the crystal structures of OXA1–OXA3

Compound	C–F···Cg	F···Cg (Å)	F···Perp (Å)	C···Cg (Å)	α∠(C–F, Cg) (°)	φ∠(C–F, π) (°)
OXA1	C20–F7···Cg2^{i}	3.302(2)	3.301	4.214(3)	125.6(1)	34.05
	C20–F9···Cg3^{ii}	3.123(2)	3.109	4.079(2)	127.5(2)	35.46
OXA2	C21–F10···Cg3^{i}	3.670(2)	3.947	3.947(2)	92.3(1)	29.16
	C21–F12···Cg3^{i}	3.642(2)	3.947	3.947(2)	93.1(2)	21.64
OXA3	C21–F11···Cg3^{i}	3.376(5)	3.276	4.592(6)	154.4(3)	61.74
	C21–F12···Cg2^{ii}	3.243(3)	3.195	3.974(5)	114.7(3)	34.26

(OXA1) i = 1/2 − x, 1/2 + y, 1/2 − z; ii = 1/2 − x, −1/2 + y, 1/2 − z. (OXA2) i = 1 − x, −y, 1 − z. (OXA3) i = −x, 1 − y, 1 − z; ii = −1 + x, 1/2 − y, −1/2 + z.
The Cg numbers refer to the ring centre-of-gravity numbers given in Fig. 1.

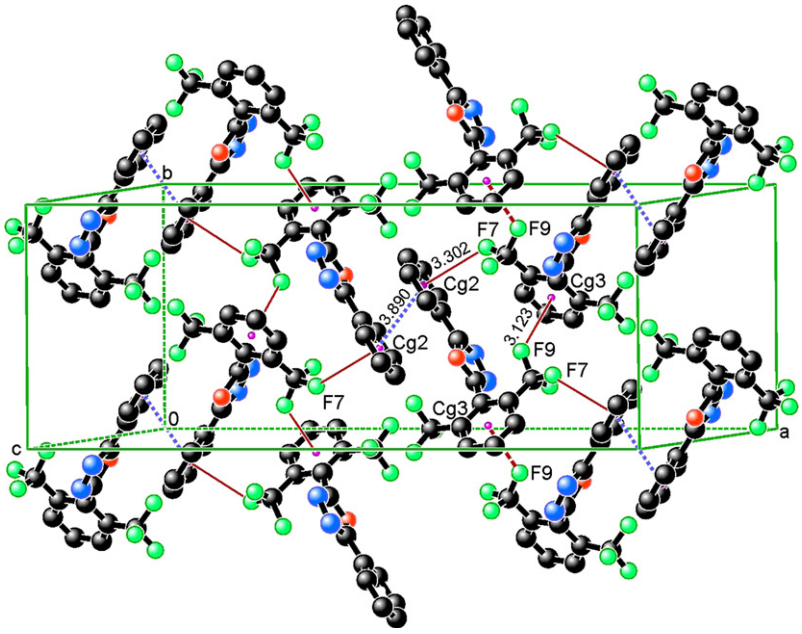

Fig. 3. Intermolecular interactions in the crystal structure of OXA1. π–π interactions are indicated via dotted lines, C–F···π interactions via solid lines. Intramolecular interactions are excluded for clarity.

intramolecular C–F···π interactions between the CF_3 group and the oxadiazole ring are formed only in the case of double *ortho* substitution. The energy gain obtained by the rotation of the mono-CF_3 substituted phenylene ring against the plane of the oxadiazole ring is not sufficient to induce a stronger conformation change.

3.2. Intermolecular interactions

In the following the crystal structures of OXA1–OXA3 will be discussed separately focused on the different kinds of intermolecular interactions and resulting packing motifs.

The compound OXA1 crystallizes in the space group C2/*c*. The basic building block of its crystal structure includes a dimer of two oxadiazole molecules which are connected via π–π electron interactions between two unsubstituted phenyl rings of adjacent molecules (Cg2···Cg2), symmetrically related by the inversion centre in ⟨0 0 0⟩. The dimer is also linked to adjacent molecules via C–F···π interactions (C20–F7···Cg2, C20–F9···Cg3; see Table 3 for details). The involved molecules are symmetrically related by a 2_1-rotation axis running parallel to the *b* axis. The intermolecular interactions lead to the formation of layers in the (−1 0 1) plane stacked along the *c* axis, as illustrated in Fig. 3. These layers are interconnected via weak π–π electron interactions between the CF_3-substituted phenylene rings (Cg3···Cg3). The values for the π–π electron interactions are given in Table 5. Short F–F contacts and intermolecular C–H···F interactions were not observed.

The molecular packing of OXA2 is shown in Fig. 4. This compound crystallizes in the monoclinic space group $P2_1/c$. Along the *c* axis stacks of head to tail oriented OXA2 molecules, generated by the c glide plane parallel to the a–c plane are formed, providing the basis for π–π electron interactions between neighboring 2,6-bis(trifluoromethyl) phenylene rings (Cg3···Cg3). The separation of the molecular planes, 3.856(2) Å (Fig. 4), indicates weak π–π interactions. The values for the interactions are given in Table 5. Weak stacking interactions between adjacent (trifluoromethyl)phenylene rings complete the intermolecular interactions in the crystal structure. The associated values are given in Table 5. The close intermolecular F–F contacts, 2.748(2) Å (assuming a van der Waals radius of 1.47 Å for the fluorine atom [28]), resulting from the packing arrangement,

Table 5
π–π electron interactions in the crystal structures of OXA1 and OXA2

Compound	CgI···CgJ	Cg–Cg (Å)	CgI Perp (Å)	CgJ Perp (Å)	α (°)
OXA1	Cg2···Cg2^{i}	3.890(2)	3.461	3.461	0.0
	Cg3···Cg3^{ii}	4.090(2)	3.712	3.712	0.0
OXA2	Cg2···Cg2^{i}	4.169(2)	3.680	3.696	3.32
	Cg2···Cg2^{ii}	4.169(2)	3.696	3.680	3.32
	Cg3···Cg3^{iii}	3.856(2)	3.701	3.701	0.03

(OXA1) i = 1 − *x*, 1 − *y*, 1 − *z*; ii = 1/2 − *x*, 3/2 − *y*, −z. (OXA2) i = *x*, 1/2 − *y*, 1/2 + z; ii = *x*, 1/2 − *y*, −1/2 + *z*; iii = 1 − *x*, −*y*, 2 − *z*.
The Cg numbers refer to the ring centre-of-gravity numbers given in Fig. 1.

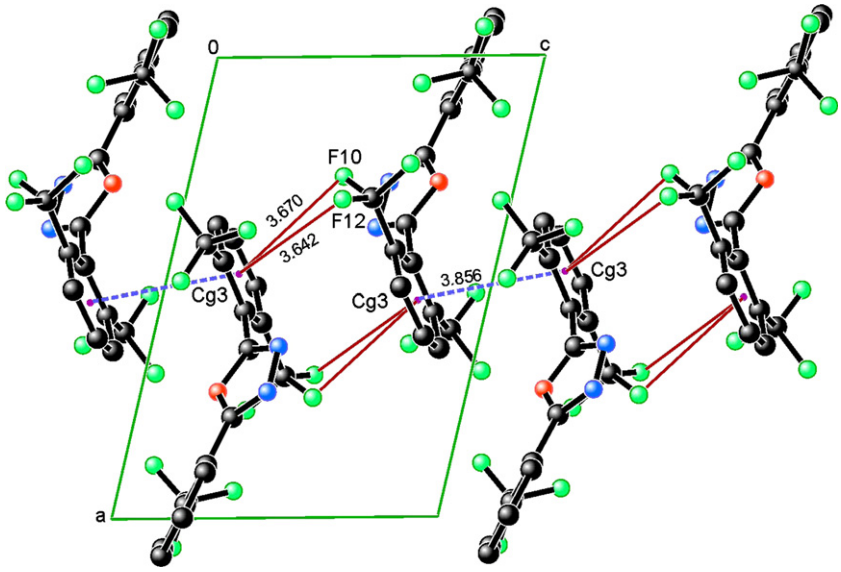

Fig. 4. Molecular packing in the crystal structure of OXA2 viewed along the *b* axis. π–π interactions are indicated via dotted lines, C–F···π interactions via solid lines. Intramolecular interactions are excluded for clarity.

are tolerated by the structure. Intermolecular C–H···F interactions are not observed.

Compound OXA3 (Fig. 5) crystallizes in the space group $P2_1/c$. The crystal structure is composed of a dimeric unit consisting of two OXA3 molecules, symmetrically dependent via inversion centres. Fig. 5 illustrates the occurrence of C–F···π interactions (C21–F11···Cg3) between the OXA3 molecules. In the b–c plane neighboring dimers are connected via additional C–F···π interactions (C21–F12···Cg2), as depicted in Fig. 5. The numerical values are given in Table 3.

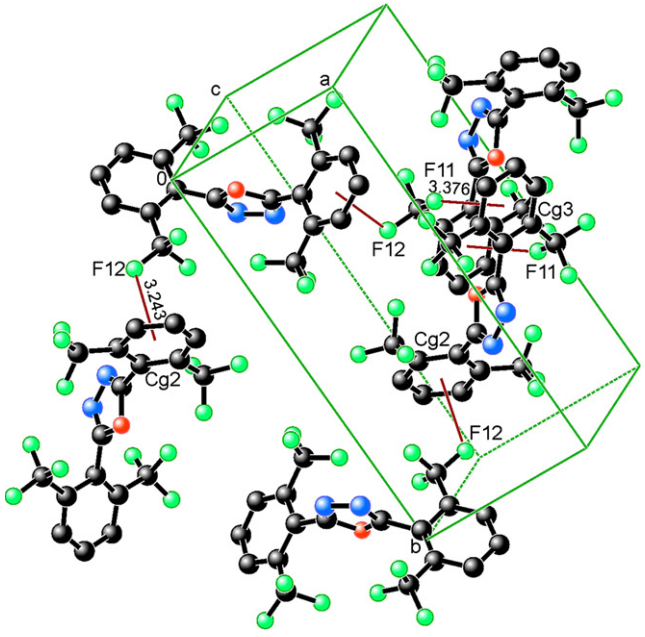

Fig. 5. Intermolecular interactions in the crystal structure of OXA3. Molecular layers in the crystal structure of OXA3 parallel to the (−201) plane. C–F···π interactions are represented via solid lines.

As a consequence of the conformational features short F–F contacts of 2.866(4) Å are detected between adjacent molecules. Similarly, as observed for OXA1 and OXA2 no intermolecular C–H···F interactions occur.

4. Conclusion

The organo halogene compounds are known to generate structural motifs via intermolecular interactions like C–H···X, X···X, C–X···π (X = Cl, Br, I). Detailed CSD [29] and PDB [15] investigations concerning the role of C–X···π interactions (X = F, Cl, Br, I) showed, that the tendency of the formation of C–X···π interactions is higher in case of fluorine than in those of the other halogens. In this work, we investigated three different diphenyl-oxadiazole molecules containing trifluoromethyl *ortho* substitutents. First of all, this substitution considerably influences the molecular conformation. A trifluoromethyl group in *ortho* position of the phenylene ring leads to the rotation of this ring with respect to the central oxadiazole ring. However, the rotation of the second, doubly substituted ring is unaffected of this, keeping a nearly constant torsion angle to the oxadiazole ring. Thus, only weakly or not conjugated molecules result indicated by the interring bonds between the different aromatic rings. And, additionally, this molecular twist leads to the formation of intramolecular CF···π interactions with the oxadiazole ring. Such intramolecular C–F···π interactions can be observed in all the compounds, but, interestingly, only in the case of a doubly substituted phenylene ring. A single CF_3 group is not involved in such interactions. Additionally, also intramolecular C–H···F interactions between neighbored atoms in a molecule are found for every investigated compound.

Usually, the crystal structures of diphenyl-oxadiazoles are dominated by strong π–π stacking interactions. Such

interactions are only found in the case of OXA1 and OXA2 although being relatively weak. In the crystal structure of the fully *ortho* substituted compound OXA3 the π–π stacking interactions are replaced by C–F⋯π interactions. Generally, the tendency to form π–π interactions is reduced with increasing *ortho* substitution that complicates a stack-like arrangement. It is noteworthy, that the C–F⋯π interactions are also observed in compound OXA1. Here, and in OXA3 they provide the stability of the packing motif. Contrary to possible assumptions based on common synthons, that strongly twisted molecules with aromatic rings could form T-like arrangements with corresponding interactions, such structures are not found for the investigated compounds.

With increasing substitution also the number of close F–F contacts increases. Such interactions are not observed in OXA1 but in OXA2 and OXA3. No intermolecular C–F⋯H hydrogen bonds were observed in the crystal structures of the three compounds. Since fluorine can only act as a hydrogen-bond acceptor, the lack of strong hydrogen donors within the molecules might be a reason. Therefore, the observed C–F⋯π interactions and close F–F contacts as main intermolecular interactions in the studied compounds obviously provide the stability to form molecular assemblies in absence of any other strong intermolecular forces as i.e. hydrogen bonds like in the case of OXA3. The strength and the number of these intermolecular interactions, the packing motifs, and thus the crystal structures clearly depend on the number of trifluormethyl substituents.

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